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Synthesis and Characterization of Silyldichloramines, their Reactions with F⁻ Ions, Stability of N₂Cl₂ and NCl₂⁻, and Formation of NCl₃ (PREPRINT)

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Abstract: Only two silyldichloramines, $(C_6H_5)_3SiNCl_2$ and $(CH_3)_3SiNCl_2$, have been reported in the literature. The synthesis of the former was successfully repeated, and its structure was established by single crystal X-ray diffraction and vibrational spectroscopy. Attempts to prepare $(CH_3)_3SiNCl_2$ were unsuccessful, however, a new trialkylsilyldichloramine, $t\text{-BuMe}_2\text{Si-NCl}_2$, was prepared and characterized by Raman and multinuclear NMR spectroscopy. The reaction of $t\text{-BuMe}_2SiNCl_2$ with $(CH_3)_4NF$ in CHF_3 solution at -78 °C, followed by removal of all volatile products at -30 °C, produced the expected $t\text{-BuMe}_2SiF$ by-product and a white solid consisting of NCl_3 absorbed on Me_4NCl. The NCl_3 could be reversibly desorbed from the substrate and was identified as a neat liquid at room temperature by Raman spectroscopy. The observed final reaction products are consistent with the formation of an unstable $N(CH_3)_4^+NCl_2^-$ intermediate which decomposes to $N(CH_3)_4^+Cl^-$ and NCl molecules which can dimerize to N_2Cl_2. Theoretical calculations confirm that NCl_2^- can readily lose Cl^- and that N_2Cl_2 also possesses a low barrier towards loss of N_2 to give chlorine atoms and, thus, can account for the formation of NCl_3.

Introduction

Chloramines are important intermediates in the industrial production of hydrazine by the Raschig process and hold potential as precursors for the synthesis of azidamines. However, neat chloramines are highly unstable and often can decompose explosively. Therefore, relatively little is known about these compounds. Chloramine chemistry had its ominous beginning in 1811 when Dulong lost three fingers and an eye during the discovery of NCl_3. Almost a century later in 1908, a second nitrogen chloride, chlorine azide, was observed by Raschig when he added acetic acid to equimolecular amounts of sodium azide and sodium hypochlorite in aequeous solution. Another 12 years went past before Marckwand and Wille added NH_2Cl to the nitrogen chloride family, followed by the synthesis of $NHCl_2$ in 1929 by Chapin.[1,2] It is noteworthy that almost another half a century went by until in 1977 and 1990 the first nitrogen chloride ions, $ONCl_2^+$ and NCl_4^+, were reported,[3,4] but so far the synthesis of neither one of these two compounds has been confirmed.

Very recently we reported the syntheses and characterization of $NH_3Cl^+M^-$ salts (M = BF_4, AsF_6, SbF_6) in which the explosiveness and thermal instability of the parent molecule NH_2Cl were circumvented by using an organosilicon derivative, $(Me_3Si)_2NCl$, as starting material.[5] Generally, covalent R_3Si-X bonds can be readily cleaved by strong acids and nucleophiles, such as fluoride ions. In the case of $(Me_3Si)_2NCl$, the silicon nitrogen bond was cleaved by anhydrous HF in the presence of Lewis acids, resulting in the formation of the desired NH_3Cl^+ salts (eq 1).

$$(R_3Si)_2NCl + 3\ HF\ +\ MF_5\ \longrightarrow\ NH_3Cl^+MF_6^- + 2\ R_3SiF \qquad (1)$$

In this paper, we describe a modification of this approach which has the potential of generating nitrogen chloride anions instead of cations by using the strongly basic fluoride anion in place of the HF/MF_5 super-acid system as the cleaving agent (eq 2).

$$R_3SiNCl_2 + Me_4N^+F^- \longrightarrow Me_4N^+NCl_2^- + R_3SiNF \qquad (2)$$

Although the chlorination of amine complexes of platinum (IV+) affords covalently bonded NCl_2 ligands,[6] and numerous free pseudo-halide amide anions, NX_2^- (X = SO_2F,[7] SO_2CF_3,[8] SO_2Cl,[9] CF_3,[10] SF_5,[11] TeF_5,[12] CN[13]), are known, the free NCl_2^- anion is unknown.

Surprisingly, little was known about the required triorganylsilydichloramines starting materials. To the best of our knowledge, only two examples of this class of compounds, triphenylsilyldichloramine[14] and trimethylsilyldichloramine,[15] have previously been reported. Therefore, the synthesis of these compounds was reexamined.

Experimental Section

*Caution! Neat chloramines are highly unstable and often can decompose explosively. They should be handled on a small scale with appropriate safety precautions. **Especially, the handling of neat NCl_3 has led in the past to serious injuries!***

Materials and Apparatus. Reactions were carried out in Teflon-FEP ampules that contained Teflon coated magnetic stirring bars and were closed by stainless steel valves. The valves were attached to the ampules through stainless steal T-fittings. The valve was attached to the horizontal part of the T and the top end of the T was closed by a removable stainless steal cap allowing the addition of solids or liquids to the ampule under dry nitrogen conditions. Volatile materials were handled on a Pyrex glass vacuum line equipped with grease-free Kontes glass-Teflon valves. Nonvolatile solids were handled in the dry nitrogen atmosphere of a glove box.

Infrared spectra were recorded on a Midac M Series FT-IR spectrometer using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded in the range 4000-80 cm^{-1} on a Bruker Equinox 55 FT-RA 106/S spectrometer using a Nd-Yag laser at 1064 nm. Pyrex melting point capillaries, glass NMR or 9 mm Teflon-FEP tubes were used as sample containers. Nuclear magnetic resonance spectra were recorded unlocked on a Bruker AMX 500 NMR spectrometer at room temperature. The ^{1}H, ^{13}C, ^{29}Si (^{14}N) NMR spectra were referenced to external samples of neat TMS, (neat nitromethane).

The Ph_3SiNCl_2 was prepared using the literature method.[14] Diethylether was dried over sodium. NH_3 (Aldrich, anhydrous, 99.99%), CF_3H (Matheson Co.), Ph_3SiNH_2 (Aldrich, 97%), *tert*-$BuMe_2SiCl$ (Aldrich, 97%) and *tert*-BuOCl (TCI, 98%) were used without further purification. Tetramethylammonium fluoride tetrahydrate (Aldrich, 98%) was dehydrated by a literature method.[16]

Crystal Structure Determination of Ph_3SiNCl_2. (a) Collection and Reduction of X-ray Data. The crystal used in this study had the dimensions $0.155 \times 0.152 \times 0.106$ mm^3. X-ray diffraction data were collected using a Bruker 3-circle platform diffractometer, equipped with a SMART APEX CCD (charge coupled device) detector with the χ-axis fixed at 54.74° (using the program SMART[17]), and using MoK_{α} radiation ($\lambda = 0.71073$ Å) from a fine-focus tube. The diffractometer was equipped with a cryo-cooler from CRYO Industries for low-temperature data collection using controlled liquid nitrogen boil off. Cell constants were determined from 60 ten-second frames at 130 °K. A complete hemisphere of data was collected up to a resolution of 0.75 Å. Processing was carried out by using the program SAINT,[18] which applied Lorentz and polarization correction to three-dimensionally integrated diffraction spots. The program

SADABS[19] was used for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections.

   (b) Solution and Refinement of the Structure. All data were processed using the SHELXTL package (version 5.1)[20] for structure determination, refinement, and molecular graphics. The XPREP program was used to confirm the unit cell dimensions and the crystal lattices. The structure was solved by the direct method. Successive difference Fourier synthesis revealed all atoms. The structure was refined by the least squares method on F^2. All atoms except hydrogen were refined anisotropically. For the anisotropic displacement parameters, the U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

   Raman data for Ph_3SiNCl_2 in cm^{-1} (rel. Int.). 3174 (3), 3134 (6), 3054 (100), 2998 (3), 2978(3), 2958 (4), 2894 (1), 2851 (1), 2820 (<0.5), 2773 (<0.5), 2685 (<0.5), 2596 (1), 2524 (1), 2424 (1), 1589 (42), 1568 (9), 1482 (1), 1429 (2), 1336 (2), 1309 (1), 1188 (8), 1160 (11), 1115 (1), 1102 (11), 1071 (1), 1028 (28), 999 (87), 986 (1), 923 (1), 858 (2), 828 (14), 745 (1), 715 (3), 688 (16), 678 (2), 619 (6), 513 (11), 446 (12), 437 (4), 399 (<0.5), 391 (<0.5), 329 (10), 308 (23), 250 (3), 238 (17), 220 (6), 212 (2), 179 (1), 169 (32), 121 (3), 95 (83), 79 (7).

Preparation of t-BuMe$_2$SiNH$_2$. In a variation of the published literature methods,[21,22] a solution of 15.79g (119.48 mmole) of t-BuMe$_2$SiCl in ca. 50 mL diethylether was pressurized in a 200 mL flask with excess anhydrous ammonia and stirred overnight at room temperature to ensure the completion of the reaction. The reaction mixture was then cooled to -196 °C, and the volatile products, solvent and t-BuMe$_2$SiNH$_2$, were separated by fractional condensation by pumping them, on warm-up to room temperature, through two cold traps kept at -24 (CCl$_4$ slush bath) and -196 °C. A glass-wool plug was placed inside the connector between the reaction vessel and the -24 °C cold-trap, ensuring that none of the NH$_4$Cl by-product was swept from the reactor into the

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cold trap. The -24 °C trap contained the desired t-BuMe$_2$SiNH$_2$ as a white, crystalline solid in better than 90% yield. The purity of the t-BuMe$_2$SiNH$_2$ was verified by Raman and NMR spectroscopy.

Preparation of t-BuMe$_2$SiNCl$_2$. By analogy with the method published for the preparation of Ph$_3$SiNCl$_2$,[14] t-BuOCl (15.914g, 146.58 mmol) was added drop-wise in the dark to an ice-cooled stirred solution of t-BuMe$_2$SiNH$_2$ (8.776g, 66.38 mmol) in dry diethylether. The solution turned immediately yellow, but no precipitate was formed as in the case of Ph$_3$SiNCl$_2$, because, contrary to Ph$_3$SiNCl$_2$, t-BuMe$_2$SiNCl$_2$ is soluble in diethylether. The solvent was pumped off between -78 and -30 °C. Because the volatilities of t-BuMe$_2$SiNCl$_2$ and t-BuOH, the by-product formed in the reaction, are similar, further pumping on the residual t-BuMe$_2$SiNCl$_2$/t-BuOH mixture at RT was required for the isolation of pure, highly viscous t-BuMe$_2$SiNCl$_2$ (13.18 mmol, ~20 %). Most of the product was lost during this procedure, indicating that t-BuOH has only a slightly higher volatility than t-BuMe$_2$SiNCl$_2$. The isolated yield of t-BuMe$_2$SiNCl$_2$ could certainly be improved by the use of better separation techniques. The purity of the product was continuously monitored by Raman and NMR spectroscopy.

Raman data for t-BuMe$_2$SiNCl$_2$ in cm^{-1} (rel. Int.). 2964 (57), 2931 (64), 2905 (100), 2864 (68), 2781 (10), 2713 (7), 1464 (14), 1445 (12), 1409 (5), 1401 (5), 1365 (3), 1256 (3), 1213 (14), 1184 (5), 1013 (3), 1005 (3), 941 (7), 832 (9), 819 (16), 779 (11), 745 (3), 676 (22), 578 (26), 463 (27), 438 (17), 399 (7), 365 (7), 354 (9), 332 (19), 305 (17), 218 (24), 168 (12), 148 (11), 123 (11), 83 (15).

Reaction of t-BuMe$_2$SiNCl$_2$ with Me$_4$NF and Generation of NCl$_3$. In a typical experiment, t-BuMe$_2$SiNCl$_2$ (0.607g, 3.03 mmol) was loaded with a pipette into one of the above described Teflon-FEP ampules. To exclude moisture, this operation was carried out in dry

nitrogen streams, which were passed through the t-BuMe$_2$SiNCl$_2$ storage vessel and the Teflon ampule. The ampule was then cooled to -196 °C, evacuated, and a layer of CF$_3$H was condensed in at this temperature on the vacuum line. An equimolar amount of Me$_4$NF was added to the frozen mixture in a stream of dry nitogen, followed by an additional layer of CF$_3$H. The mixture was then warmed to -78 °C and vigorously stirred. The reaction was stopped when the yellow color of t-BuMe$_2$SiNCl$_2$ had disappeared. The solvent CF$_3$H was pumped off at -78 °C, and a stoichiometric amount of t-BuMe$_2$SiF was removed between -30 and -20 °C. At this temperature, the solid residue consisted only of NCl$_3$ absorbed on Me$_4$NCl. Warming the solid to room temperature resulted in the slow reversible release of NCl$_3$.

Results and Discussion

      Synthesis and Properties of Ph$_3$SiNCl$_2$. Of the two previously reported triorganylsilyl-dichloramines, triphenylsilyldichloramine[14] and trimethylsilyldichloramine[15], only the latter would be volatile enough to allow easy low-temperature product separation from other nonvolatile reaction products. However, our efforts were unsuccessful to repeat the previously described[14] preparation of this compound. Instead of the required unstable (CH$_3$)$_3$SiNH$_2$ intermediate, only [(CH$_3$)$_3$Si]$_2$NH was formed which, upon chlorination, produced [(CH$_3$)$_3$Si]$_2$NCl.[5] Therefore, the preparation of the triphenylsilyldichloramine was reexamined (eq 3).

$$Ph_3SiNH_2 + 2\ t\text{-}BuOCl \xrightarrow{Et_2O} Ph_3SiNCl_2 + 2\ t\text{-}BuOH \qquad (3)$$

The compound was successfully prepared and characterized by its X-ray crystal structure (Figure 1, Tables 1-3) and Raman spectrum (Figure 2) because previously only its melting point and proton NMR spectrum had been reported.[14]

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Ph_3SiNCl_2 crystallizes in the triclinic space group *P-1*. The most interesting part of the molecule (Figure 1) is the nitrogen environment, which is close to tetrahedral with Cl-N-Cl and Cl-N-Si bond angles of 108.4(1) and 112.1(1) °, respectively. The increased repulsion from the bulky phenyl groups and the sterically active, free valence electron pair on the nitrogen atom are responsible for the relatively long silicon-nitrogen distance of 181.2(2) pm. The N-Cl bond lengths of 173.8(2) and 175.4(2) pm are similar to those found in $CH_3C_6H_4SO_2NCl_2$ and $CH_3SO_2NCl_2$.[23, 24] The bond distances and angles of the triphenylsilyl group are as expected.

No attempt was made to completely assign the Raman spectrum because of its complexity due to the triphenylsilyl group. However, a comparison between the Raman spectra of the Ph_3SiNH_2 starting material and the Ph_3SiNCl_2 product (Figure 2) demonstrates that, upon chlorination, the following very intense, new bands at 688, 513, 446, and 437 cm^{-1} appear in the region of the $SiNCl_2$ stretching vibrations. Based on our theoretical calculations and normal coordinate analysis, these skeletal modes are strongly mixed. The 688 cm^{-1} mode is a mixture of Si-N and antisymmetric NCl_2 stretching and the 513 and 446/437 cm^{-1} modes are out-of-phase and in-phase combinations, respectively, of Si-N and symmetric NCl_2 stretching. For highly characteristic NCl_2 vibrations, the expected frequency separation between antisymmetric and symmetric NCl_2 stretching would be much smaller and be of the order of 20-40 cm^{-1}.

Synthesis and Properties of t-BuMe$_2$SiNCl$_2$. Since our repeated efforts to duplicate the reported[15] preparation of trimethylsilyldichloramine failed, and the corresponding triphenylsilyl compounds were not volatile enough for our purposes, the previously unknown *tert*-butyl-dimethylsilyldichloramine was prepared according to eq 3.

$$t\text{-BuMe}_2\text{SiNH}_2 + 2\ t\text{-BuOCl} \xrightarrow{\text{Et}_2\text{O}} t\text{-BuMe}_2\text{SiNCl}_2 + 2\ t\text{-BuOH} \qquad (3)$$

Unfortunately, the volatility of the dichloramine is similar to that of the by-product t-BuOH, rendering the separation of the two compounds difficult and resulting in low isolated yields. At room-temperature, the moisture sensitive t-BuMe$_2$SiNCl$_2$ is a tacky yellow solid with a very intense odor and mp of ~25-30 °C. It cannot be distilled without decomposition. Storage for a prolonged period of time at RT, especially under the influence of light, resulted in the formation of t-BuMe$_2$SiCl. Its purity was ascertained by Raman and NMR spectroscopy. The ^{1}H, ^{13}C, ^{29}Si and ^{14}N NMR spectroscopic data of neat t-BuMe$_2$SiNCl$_2$ are listed in Table 4. The ^{1}H, ^{13}C and ^{29}Si NMR chemical shifts are located in the region expected for the t-BuMe$_2$Si group. The broad ^{14}N resonance for -NCl$_2$ at -280 ppm ($\Delta\nu_{\frac{1}{2}}$ = 770 Hz) lies within our expectations.[25]

The Raman spectra of t-BuMe$_2$SiNCl$_2$ (upper) and of t-BuMe$_2$SiNH$_2$ (lower trace) are shown in Figure 3. While the t-BuMe$_2$Si-skeleton results again in complex vibrational spectra, a comparison of the two spectra reveals for the NCl$_2$ compound strong Raman bands at 676, 463 and 438 cm^{-1}. These are attributed, similarly to Ph$_3$SiNCl$_2$, to NCl$_2$ motions which are strongly coupled to the skeletal Si-NC$_3$ modes. In support of this interpretation, a normal coordinate analysis was carried out for the most simple, but unknown, silyldichloramine, H$_3$SiNCl$_2$. The calculated structure is shown in Figure 4, and the results from the normal coordinate analysis are summarized in Table 5. It can be seen from the potential energy distribution that, even in this relatively simple molecule, the skeletal modes are strongly mixed. For example, the maximum contribution from symmetric NCl$_2$ stretching (S7) to any single mode does not exceed 38% and that from antisymmetric NCl$_2$ stretching (S12) is even smaller with 18%. This analysis demonstrates the fallacy of assigning, for these compounds, characteristic NCl$_2$ bands.

Reaction of *t*-BuMe₂SiNCl₂ with Tetramethylammoniumfluoride. The cleavage of the Si-N bond in t-BuMe$_2$SiNCl$_2$ by Me$_4$NF (eq 2) was studied in CHF$_3$ solution[16] at -78 °C. The solvent was pumped off at this temperature, and the t-BuMe$_2$SiF by-product, which was formed in quantitative yield, was removed at -25 °C. The latter was identified by mass-balance and IR, Raman and NMR spectroscopy. The low-temperature Raman spectrum (Figure 5) of the solid residue showed bands due to Me$_4$NCl and intense new bands at 635, 617, 611, 540, 356, and 276 cm^{-1}. Clearly, the number and frequencies of these bands were incompatible with the presence of an NCl$_2^-$ anion which, based on our theoretical predictions at the CCSD(T)/cc-pvtz level, should exhibit only three bands with frequencies of about 579, 526, and 258 cm^{-1}. The identity of the species, absorbed on the Me$_4$NCl, was established by warming the solid to room temperature and collecting the volatiles at -196 °C. Based on their Raman spectra, the solid residue consisted of Me$_4$NCl, while the volatile product, a yellow liquid at room temperature, was pure NCl$_3$.[26-29] Our Raman spectrum of liquid NCl$_3$ (Figure 6) is the first well defined spectrum of the neat substance. Previously, only a partial spectrum of poor quality had been reported by Hendra and Mackenzie.[27] All these Raman data together with their assignments are listed in Table 6. To clarify the composition of the species absorbed on Me$_4$NCl at -25°C, the collected NCl$_3$ was condensed back onto the Me$_4$NCl, and the low-temperature Raman spectrum was rerecorded. The spectrum was identical to the initial one and shows that the absorbed species is indeed NCl$_3$ and that the absorption and desorption are reversible. The marked differences in the spectra of absorbed and neat NCl$_3$ are attributed to crystal splittings and solid state effects.

A plausible explanation for the overall process which led to the formation of Me$_4$NCl and NCl$_3$ is given by the following equations:

$$t\text{-BuMe}_2\text{SiNCl}_2 + [\text{Me}_4\text{N}]^+\text{F}^- \longrightarrow [\text{Me}_4\text{N}]^+[\text{NCl}_2]^- + t\text{-BuMe}_2\text{SiF} \tag{5}$$

$$[\text{Me}_4\text{N}]^+[\text{NCl}_2]^- \longrightarrow \text{Me}_4\text{NCl} + \text{NCl} \tag{6}$$

$$2\,\text{NCl} \longrightarrow \text{N}_2\text{Cl}_2 \tag{7}$$

$$3\,\text{N}_2\text{Cl}_2 \longrightarrow 2\,\text{NCl}_3 + 2\,\text{N}_2 \tag{8}$$

$$3\,t\text{-BuMe}_2\text{SiNCl}_2 + 3\,\text{Me}_4\text{NF} \longrightarrow 3\,\text{Me}_4\text{NCl} + \text{NCl}_3 + \text{N}_2 + 3\,t\text{-BuMe}_2\text{SiF} \tag{9}$$

The proposed sequence of reactions is supported by theoretical calculations. Although the NCl_2^- anion is vibrationally stable, its energy barrier toward the loss of a chloride ion is predicted to be low. The thermodynamically most favorable dissociation path for NCl_2^- is the loss of a Cl^- ion and spin-forbidden formation of ground state ($^3\Sigma^-$) NCl, whereas the lowest energy spin-allowed pathway leads to formation of excited state ($^1\Delta$) NCl. Full valence complete active space self-consistent field (CASSCF) calculations[30] with the 6-311+G(2df) basis set[31] were performed to map out the lowest dissociative singlet and triplet potential energy surfaces and to determine the point at which they intersect. These calculations, which include nondynamical correlation but omit dynamical correlation effects, show that formation of excited ($^1\Delta$) NCl plus chloride is endothermic by 16.5 kcal mol^{-1}, whereas formation of ground state ($^3\Sigma^-$) NCl + chloride is exothermic by 15.1 kcal mol^{-1}. At the point where the lowest singlet and triplet potential energy surfaces intersect, the partially dissociated NCl_2^- species has N-Cl bond distances of 1.727 and 2.177 angstroms and a Cl-N-Cl bond angle of 105.6 degrees, and is 6.9 kcal/mol higher in energy than the NCl_2^- local minimum. Therefore, assuming the presence of sufficient spin-orbit coupling in the vicinity of the intersection, intersystem crossing from the

initial singlet state to the triplet electronic state could lower the effective barrier to dissociation to 6.9 kcal mol^{-1}.

These results are *qualitatively* similar to the previous calculations by Milburn, Rodriques and Hopkinson[32] at the MP2/6-311++G(2df,p) and QCISD(T)/6-311++G(2df,p) levels (which include dynamical correlation but do not explicitly include effects of nondynamical correlation), for which the endothermicities toward Cl$^-$ loss are only 37.5 and 7.3 kcal mol^{-1} on the spin allowed singlet surface (with formation of excited ($^1\Delta$) NCl) and spin-forbidden triplet surface (with formation of ground state ($^3\Sigma^-$) NCl,) respectively.

Out of the three possible isomers of N_2Cl_2, only the *cis-* and the *trans-* isomers are vibrationally stable, while the *iso-* isomer is not a minimum on the potential energy surface. As has been shown in a previous high level study by Tschumper, Heaven and Morokuma,[33] the *cis-* and the *trans-* isomers of N_2Cl_2 also have very low predicted barriers to dissociation of only 7-8 kcal mol^{-1} at the CCSD(T) level and of ≤1.5 kcal mol^{-1} at the CASPT2 level and are barely bound. For comparison, we have also calculated the structures and vibrational spectra of the NCl_4^+ and NCl_2^- ions and the N_2Cl_4 and NCl_3 molecules at the CCSD(T)/cc-pvtz and MP2/6-31+G(d) levels of theory. Whereas the agreement between the CCSD(T) and MP2 calculations was quite good for all the geometries and the vibrational frequencies of the relatively well bound NCl_3 and NCl_4^+ species, there were large discrepancies between the CCSD(T) and MP2 vibrational frequencies for the N_2Cl_2 isomers and NCl_2^-, indicating that the frequency predictions for these weakly bound species require very careful high level calculations.

Conclusions. Only two silyldichloramines, $(CH_3)_3SiNCl_2$ and $(C_6H_5)_3SiNCl_2$, had previously been reported. Out of these, only the synthesis of $(C_6H_5)_3SiNCl_2$ could be duplicated, and its crystal structure was determined. The new silyldichloramine, *t*-BuMe$_2$SiNCl$_2$, was

prepared and characterized. It is shown that in these triorganylsilyldichloramines and the yet unknown H_3SiNCl_2 the NCl_2 stretching modes strongly couple to the skeletal modes, thus making it impossible to assign characteristic stretching frequencies to the NCl_2 group. The reaction of t-$BuMe_2SiNCl_2$ with $[N(CH_3)_4]^+F^-$ provides indirect evidence for the formation of the unstable intermediates, $[N(CH_3)_4]^+NCl_2^-$ and N_2Cl_2, giving rise to $[N(CH_3)_4]^+Cl^-$ and NCl_3 as the final products. The latter two compounds reversibly form a loose adduct, exhibiting a Raman spectrum which deviates significantly from that of pure NCl_3. Also, a reliable Raman spectrum of highly explosive, neat liquid NCl_3 has been recorded for the first time. Theoretical calculations for NCl_2^-, NCl_3, N_2Cl_4, NCl_4^+, and the different isomers of N_2Cl_2, support the inferred instabilities of NCl_2^- and N_2Cl_2 and demonstrate the difficulties involved in making reliable stability and property predictions for very weakly bound systems.

Acknowledgements

Supporting Information Available

CCDC 253436 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Table 1. Crystal Data for Ph_3SiNCl_2.

chemical formula	C18 H15 Cl2 N Si
fw	344.30
T, K	85(2)
space group	P-1 Triclinic
a, Å	9.073(2)
b, Å	9.797(2)
c, Å	10.1333(2)
α, deg	107.983(4)
β, deg	102.954(4)
γ, deg	96.174(4)
V, $Å^3$	819.6(3)
Z	2
ρ_{calc}, g cm^{-3}	1.395
μ, mm^{-1}	0.464
$R1$,[a] $wR2$[b] [I > 2σ(I)]	0.0391, 0.0939
$R1$,[a] $wR2$[b] (all data)	0.0453, 0.0973

[a] $R1 = (\Sigma(F_0-F_c)/F_0)$. [b] $wR2 = [\Sigma(w(F_0-F_c)^2)w/F_0^2)]^{1/2}$.

Table 2. Selected Bond Lengths [Å] and Angles [°] for Ph_3SiNCl_2.

	bond lengths [pm]		bond angles [°]
Si(1)-N(1)	181.3(2)	N(1)-Si(1)-C(1)	100.53(8)
Si(1)-C	185.7(2)-186.2(2)	N(1)-Si(1)-C(13)	104.77(8)
N(1)-Cl(1)	173.8(2)	N(1)-Si(1)-C(7)	113.84(8)
N(1)-Cl(2)	175.4(2)	C(7)-Si(1)-C(13)	111.33(8)
		C(7)-Si(1)-C(1)	113.42(8)
		C(1)-Si(1)-C(13)	112.22(8)
		Cl(1)-N(1)-Cl(2)	108.43(9)
		Cl(1)-N(1)-Si(1)	112.07(9)
		Cl(2)-N(1)-Si(1)	112.10(9)

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Ph$_3$SiNCl$_2$.

	x	y	z	U(eq)[a]
Si(1)	3696(1)	1371(1)	3032(1)	14(1)
N(1)	2559(2)	2103(2)	1794(2)	19(1)
C(1)	3041(2)	-621(2)	2029(2)	16(1)
C(2)	4077(2)	-1586(2)	1894(2)	18(1)
C(3)	3562(3)	-3067(2)	1114(2)	22(1)
C(4)	2008(2)	-3607(2)	453(2)	22(1)
C(5)	958(2)	-2671(2)	575(2)	21(1)
C(6)	1466(2)	-1197(2)	1355(2)	19(1)
C(7)	5810(2)	1992(2)	3440(2)	15(1)
C(8)	6570(2)	1792(2)	2350(2)	21(1)
C(9)	8158(2)	2237(2)	2685(2)	23(1)
C(10)	9017(2)	2895(2)	4106(2)	23(1)
C(11)	8295(2)	3094(2)	5198(2)	23(1)
C(12)	6708(2)	2639(2)	4869(2)	19(1)
C(13)	3020(2)	1976(2)	4689(2)	15(1)
C(14)	2201(2)	937(2)	5080(2)	17(1)
C(15)	1705(2)	1349(2)	6327(2)	19(1)
C(16)	2011(2)	2803(2)	7195(2)	21(1)
C(17)	2827(2)	3853(2)	6840(2)	20(1)
C(18)	3331(2)	3441(2)	5603(2)	18(1)
Cl(1)	2933(1)	4003(1)	2426(1)	31(1)
Cl(2)	2871(1)	1488(1)	79(1)	27(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 4. ^1H, ^{13}C, ^{29}Si and ^{14}N NMR Spectra of t-BuMe$_2$SiNCl$_2$.

		chem shift, δ ppm);	Δν$_{1/2}$ (Hz)
^1H	C(CH)$_3$	2.25 (s)	
	(CH$_3$)$_2$	1.53 (s)	
^{13}C	C(C̲H)$_3$	27.15 (s)	
	C̲(CH)$_3$	19.96 (s)	
	(CH$_3$)$_2$	5.81 (s)	
^{29}Si		39.8 (s)	
^{14}N		-280 (s)	770

Table 5. Vibrational Frequencies (cm^{-1}), calculated at the MP2/6-31G(d) Level, of H_3SiNCl_2 with C_s symmetry, and Mode Description derived from a Normal Coordinate Analysis.

symmetry coordinate	calcd freq	potential energy distribution (%)
S1 ν sym SiH$_3$ in phase	a' ν_1 2362	88(1), 12(2)
S2 ν sym SiH$_3$ out of phase	ν_2 2331	89(2), 10(1)
S3 δ umbrella SiH$_3$	ν_3 988	54(4), 46(3)
S4 δ sciss SiH$_2$	ν_4 973	98(4)
S5 ν SiN	ν_5 883	55(5), 28(7), 12(9), 5(8)
S6 δ rock SiH$_3$	ν_6 703	96(6), 2(8), 1(9)
S7 ν sym NCl$_2$	ν_7 485	38(7), 25(5), 22(8), 11(9), 3(6)
S8 δ sciss NCl$_2$	ν_8 299	89(8), 5(6), 3(9), 2(5)
S9 δ Si-N=Cl$_2$	ν_9 206	67(9), 24(8), 6(6), 1(7)
S10 νasym SiH$_3$	a'' ν_{10} 2375	100(10)
S11 δ as SiH$_3$	ν_{11} 995	63(11), 35(15)
S12 νasym NCl$_2$	ν_{12} 779	43(13), 29(15)(5), 18(12), 9(14)
S13 δ wag SiH$_3$	ν_{13} 653	81(13), 10(12), 7(15), 1(14)
S14 δ twist NCl$_2$	ν_{14} 218	92(15), 7(14)
S15 τ Si-N	ν_{15} 171	89(15), 10(14)

Table 6. Raman spectra of solid Me_4NCl, $Me_4NCl“\cdot\frac{1}{3}(NCl_3)”$ and neat, liquid NCl_3.

Me₄NCl at RT		Me₄NCl·NCl₃ at -25°C		NCl₃ at RT		assignments Me₄N⁺[a]	NCl₃
3026	(95)	3026	(51)				
3018	(100)	3017	(71)				
2950	(83)	2952	(51)				
		2926	(31)				
		2898	(18)				
2877	(30)	2877	(15)			νCH_3 and	
		2827	(6)			combination	
		2821	(7)			bands	
		2813	(5)				
2788	(14)	2786	(7)				
1482	(32)	1483	(21)			ν_{15}	
1477	(30)	1477	(24)			ν_6	
1455	(15)	1455	(22)			ν_2	
1401	(13)	1399	(7)			ν_{16}	
1287	(13)	1288	(15)			ν_{17}	
1191	(1)	1191	(2)			ν_7	
1181	(5)	1181	(5)			ν_{11}	
948	(36)	947	(27)			ν_{18}	
803	(1)						
759	(29)	753	(16)			ν_3	
		732	(5)[b]				
		635	(11)				$\nu_2 + \nu_4\ (b_2)^c$
		617	(49)	640	(19)		$\nu_3\ (b_2)^c$
		611	(61)				
565	(3)						
		550	(6)				
		540	(100)	539	(86)		$\nu_1\ (a_1)$
458	(13)	458	(7)			ν_{19}	
		452	(7)				
388	(5)	387	(5)			ν_8	
375	(3)	372	(5)			ν_8 or ν_{12}	
360	(3)						
		356	(70)	351	(100)		$\nu_2\ (a_1)$
		338	(5)				
		276	(61)	260	(69)		$\nu_4\ (b_2)$
109	(1)	108	(15)				
85	(9)	74	(41)	73	(11)		

[a] Based on refs 15 and 28. [b]Teflon-FEP band from the sample container. [c] Fermi resonance.

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Figure Captions

Figure 1. Structure of the Ph_3SiNCl_2 molecule. Thermal ellipsoids are shown at the 50%
probability level.

Figure 2. Raman spectra of Ph_3SiNCl_2 (upper) and Ph_3SiNH_2 (lower trace).

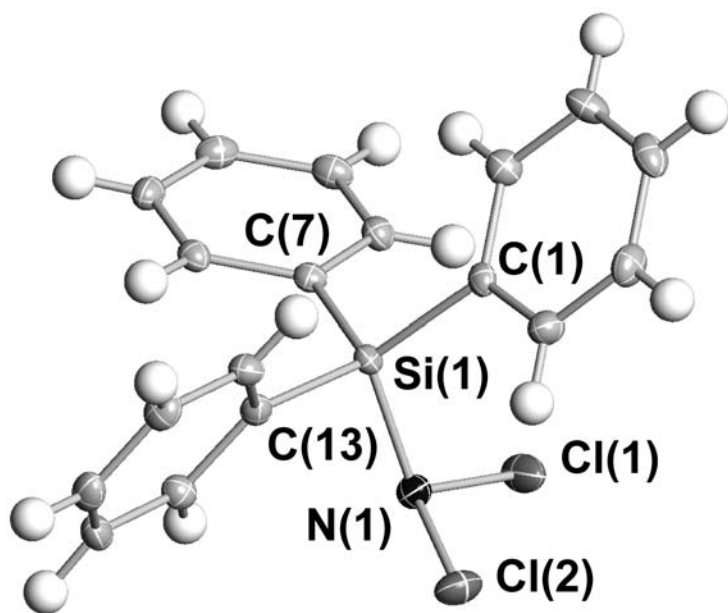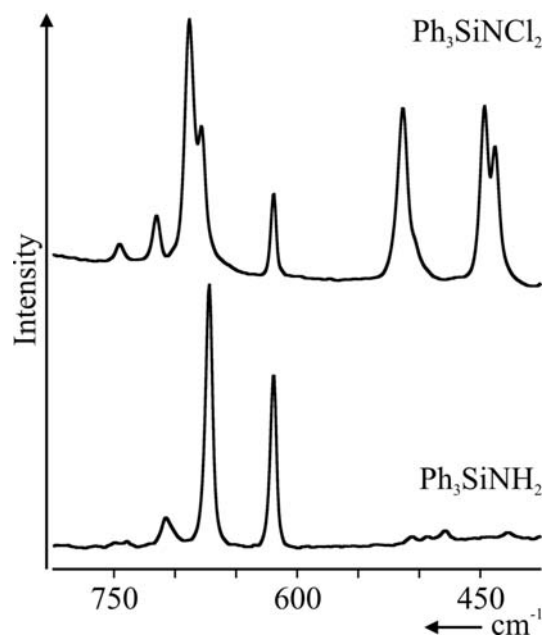Figure 3. Raman spectrum of t-$BuMe_2SiNCl_2$ (upper) and t-$BuMe_2SiNH_2$ (lower trace).

Figure 4. Geometry of H_3SiNCl_2, calculated at the MP2/6-31G(d) level; bond lengths in Å,
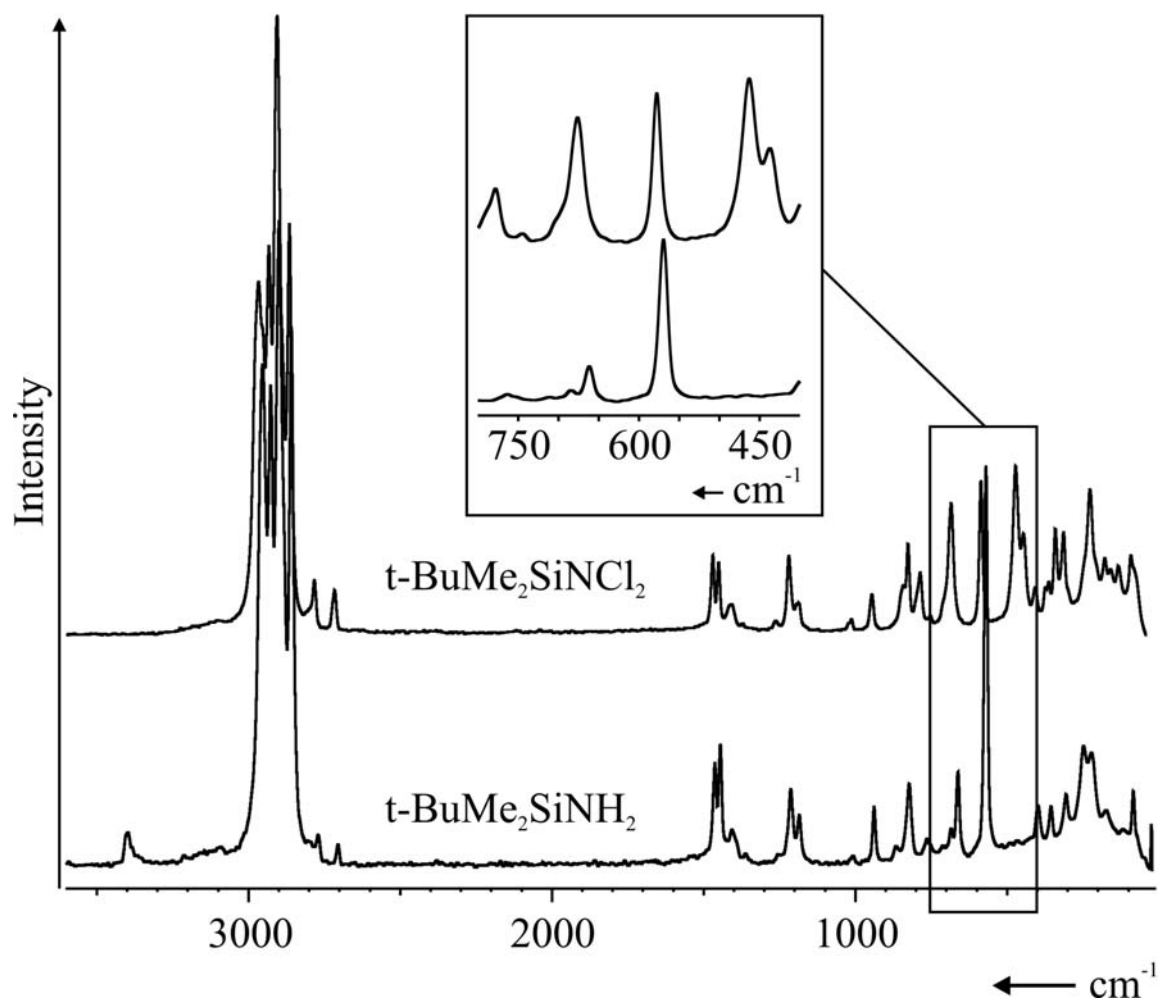angles in degrees.

Figure 5. Raman spectrum of solid Me_4NCl"$\cdot\frac{1}{3}(NCl_3)$".

Figure 6. Raman spectrum of neat NCl_3.

Figure 7. Calculated CCSD(T)/cc-pvtz geometries of NCl_2^-, NCl_3, NCl_4^+, cis-N_2Cl_2, $trans$-
N_2Cl_2, iso-N_2Cl_2, and N_2Cl_4; numbers in parentheses are the MP2/6-311+G(d) values
and numbers in brackets are experimental values; bond lengths are in Å, angles in
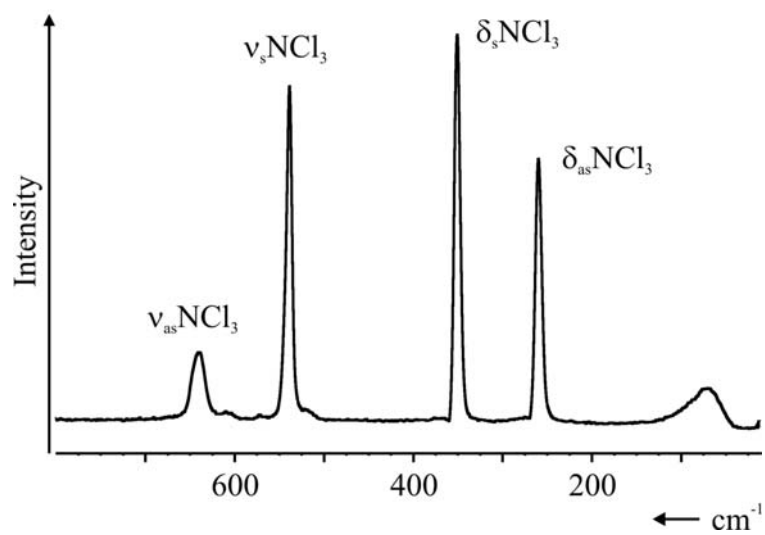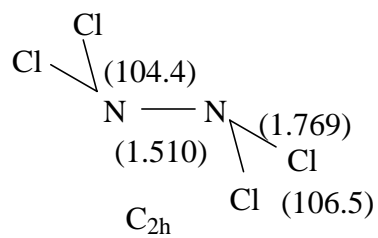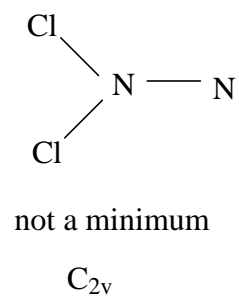degrees.

Cs
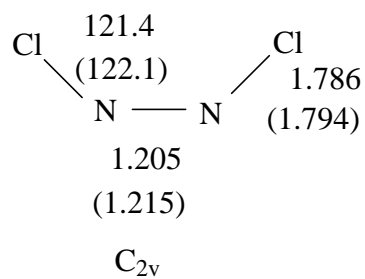
1.757 Cl7

N2 — Cl 6

| 1.810

H5 — Si1 1.476

H3

H4 1.471
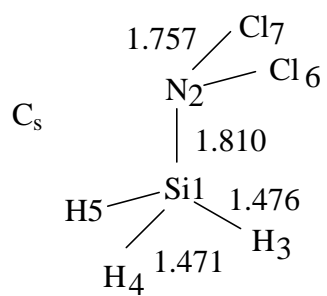
3-1-2 112.0; 4-1-2 104.9; 1-2-6 110.2;
6-2-7 110.4; 4-1-5 112.3; 4-1-3 111.2 deg
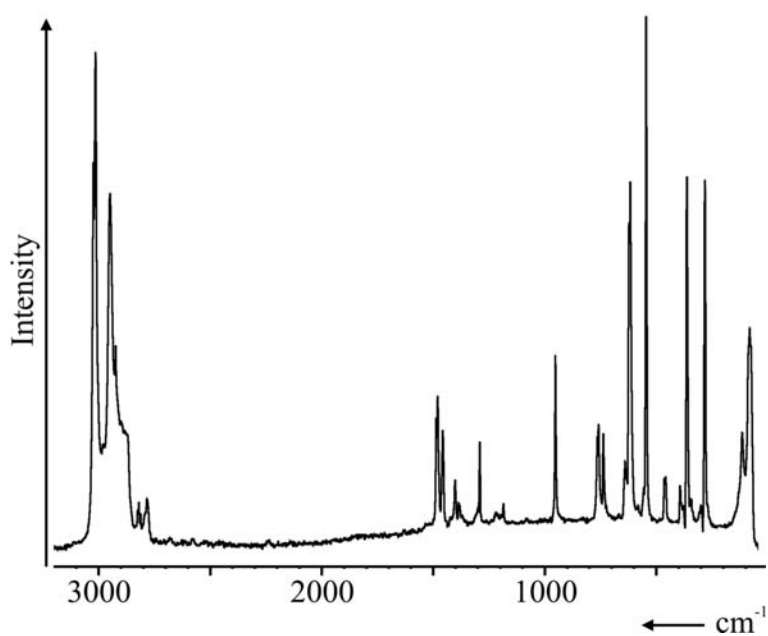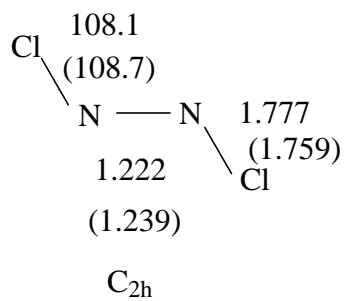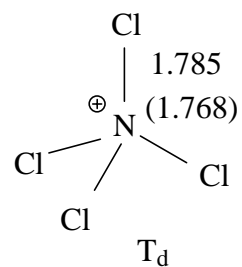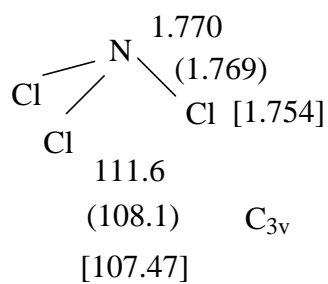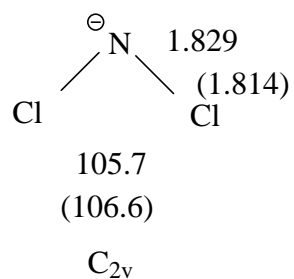
Θ
N 1.829
(1.814)
Cl   Cl
105.7
(106.6)
C$_{2v}$

1.770
N (1.769)
Cl   Cl [1.754]
Cl
111.6
(108.1)   C$_{3v}$
[107.47]

Cl
1.785
N (1.768)
⊕
Cl   Cl
Cl
T$_d$

Cl   121.4   Cl
(122.1)   1.786
N — N (1.794)
1.205
(1.215)
C$_{2v}$

Cl   108.1
(108.7)
N — N 1.777
1.222   (1.759)
Cl
(1.239)
C$_{2h}$

Cl
N — N
Cl
not a minimum
C$_{2v}$

Cl
Cl (104.4)
N — N (1.769)
(1.510)   Cl
Cl (106.5)
C$_{2h}$

Synthesis and Characterization of Silyldichloramines, their Reactions with F⁻ Ions, Stability of N_2Cl_2 and NCl_2^-, and Formation of NCl_3

Stefan Schneider*, Michael Gerken, Ralf Haiges, Thorsten Schroer, Jerry A. Boatz, Karl O. Christe[*]

The reaction of previously unknown *tert*-butyldimethylsilyldichloramine with Me_4NF results in the formation of $t\text{-}BuMe_2SiF$, Me_4NCl and surprisingly NCl_3. The generation of NCl_3 can be explained by the formation and decomposition of the unstable intermediates NCl_2^- and N_2Cl_2.